Supplemental Material

Scalable Fabrication of High-Performance Flexible Transparent Conducting Electrodes via Blade-Coating and Photonic Curing for Optoelectronic Applications

Robert T. Piper[1], Bishal Bhandari[2], Justin C. Bonner[1], Matthew Davis[3], Marisol Valdez[4], and Julia W. P. Hsu[1*]

[1]Department of Materials Science and Engineering, University of Texas at Dallas, Richardson, Texas, 75080, USA

[2]Department of Physics, University of Texas at Dallas, Richardson, Texas, 75080, USA

[3]Energy Materials Corporation, Rochester, New York, 14615, USA

[4]Department of Chemistry, University of Texas at Dallas, Richardson, Texas, 75080, USA

*Corresponding Author

Materials and Methods

Materials

The polyethylene terephthalate (PET) / Ag metal bus line (MBL) substrate material, provided by Energy Materials Corporation, is composed of PET (100 μm thick) with flexographically printed Ag MBLs. The MBLs are roughly 30 μm wide by 120 nm tall with a center-to-center pitch of ~580 μm. The isopropyl alcohol (IPA) silver nanowire (AgNW) suspension (5 mg/mL) was purchased from Sigma-Aldrich. The AgNWs have an average diameter and length of 20 nm and 12 μm, respectively. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS, Clevios 4083) solution was purchased from Heraeus Deutschland. Lead iodide (PbI_2) was purchased from TCI America. Methylammonium iodide (MAI) was purchased from GreatCell Solar. Phenyl-C_{61}-butyric acid methyl ester (PCBM) was purchased from Lumtec. N-Methylpyrrolidone (NMP) was purchased from Sigma-Aldrich. All other chemicals were purchased from Sigma-Aldrich or Fisher Scientific. All chemicals were used as received, unless otherwise stated.

TCE Fabrication

All transparent conducting electrode (TCE) fabrication processes were done in ambient conditions; the temperature (21-25 °C) and relative humidity (30-65%) were not controlled. The indium zinc oxide (IZO) solution was made by dissolving 0.4 M indium nitrate hydrate and 0.4 M zinc nitrate hexahydrate in two separate vials of 2-methoxyethanol (2-MOE)[1]. The solutions were allowed to dissolve for a minimum of 4 hrs. The day before using the solution, 0.7 M of acetylacetone and 0.6 M of ammonium hydroxide were added to both the indium nitrate and zinc nitrate solutions, separately, and mixed for ~ 12 – 15 hrs. On the day of coating, the indium nitrate

and zinc nitrate solutions were mixed in a 7:3 In:Zn volume (atomic) ratio and diluted with 2-MOE to have a total metal salts (In + Zn) concentration of 0.2 M. This IZO precursor was then mixed for at least 1 hr. The solution was filtered with a 0.2 μm polytetrafluoroethylene filter just before blade-coating.

For small-area coatings, the PET/MBL substrates were cut into 1 in (cross-web) x 3 in (down-web) rectangles. The substrates were ultrasonically cleaned in soapy water (Alconox) for 10 min followed by rinsing in deionized (DI) water, acetone, IPA, and DI water, and then blown dry with nitrogen immediately before coating. The Ag metal lines are oriented perpendicular to the down-web coating direction for all coating. A layer of AgNWs was first deposited onto the PET/MBL substrate via blade-coating (MTI Corporation MSK-AFA-III) using a blade-gap (measured from the bottom of the blade to the top of the substrate) of 510 μm and a dispensed volume of 50 μL. After blade-coating, the sample was placed on a 90 °C hot plate for 2 min to dry. Then, a layer of IZO was blade-coated on top of the AgNW layer using a blade gap of 410 μm and a dispensed volume of 25 μL. Both layers were coated at a speed of 25 mm/s. The IZO film was allowed to relax for 90 s before transferring the sample to a 90 °C hot plate for 2 min to dry. The sample was then transferred directly from the hot plate to the photonic curing tool (PulseForge Invent) and processed in air. The samples were held down onto the aluminum stage, roughly 5 mm from the xenon flash lamp, using two magnetic metal slats. The PulseForge Invent is equipped with three 950 V lamp drivers, a 1.5 kW power supply, and a 20 mm diameter x 150 mm long xenon flash lamp that provides a uniform illumination area of 75 mm x 150 mm. All samples were photonically cured using the same parameters: 300 V pulse voltage, 25 ms pulse envelope, 24 micro-pulses, 45% duty cycle, 9 pulses, 0.15 Hz pulse repetition rate, and ~ 3.5 J/cm^2 pulse fluence. After photonic curing, the sample was rinsed with DI water to remove any excess unconverted

precursor materials, followed by blowing dry with nitrogen. Finally, a second layer of IZO was then blade-coated following the same steps listed above for the first IZO layer.

Perovskite Solar Cell (PSC) Fabrication

PSCs were fabricated on the small-area hybrid TCEs and compared to two commercially available PET/TCE products: Optical Filters (OF) AG12 (https://www.opticalfiltersusa.com/products/rfi-emi-shielding) which has a PET/IMI structure and Sigma-Aldrich (SA) PET/ITO (https://www.sigmaaldrich.com/US/en/product/aldrich/639303). All device substrates used were 1 in x 1 in. The SA PET/ITO and OF AG12 were ultrasonically cleaned in soapy water, acetone, and IPA followed by rinsing in DI water and blowing dry with nitrogen. The OF and SA substrates were ultraviolet ozone (UVO) cleaned for 20 min before depositing the device layers. The small-area hybrid TCEs were cut to size and used as made without any additional cleaning or UVO treatment. The flexible substrates were then mounted onto a thin, rigid piece of glass (0.5 mm) for device fabrication and handling. The *p-i-n* device architecture was used, composed of the following layers from bottom to top: PET/TCE/PEDOT:PSS/methylammonium lead iodide ($MAPbI_3$)/PCBM/bathocuproine (BCP)/Al/Ag. The as-received acidic PEDOT:PSS (Clevios 4083) solution and IPA were mixed in a 7:3 ratio on a 50 °C hot plate for 30 minutes. For neutral PEDOT:PSS, ammonium hydroxide was added in a 5:1 ratio (PEDOT:PSS:ammonium hydroxide) and mixed for an additional 15 minutes without heating. Adding ammonium hydroxide increased the pH of the solution from 1.7 to 7. For PSCs made with the acidic PEDOT:PSS hole transport layer (HTL), the PEDOT:PSS solution was spin-coated onto the PET/TCE substrate at 4000 RPM for 30 s in a fume hood under ambient conditions. The sample was then immediately transferred into a nitrogen glovebox for thermal annealing at 120 °C for 10 min. After annealing, the sample was ready for $MAPbI_3$

deposition. For PSCs made with the neutral/acidic PEDOT:PSS bilayer, the neutral PEDOT:PSS solution was first spin-coated and thermally annealed on top of the PET/TCE substrate following the same procedures above for acidic PEDOT:PSS. Then, a layer of acidic PEDOT:PSS was spin-coated and thermally annealed on top of the neutral PEDOT:PSS to form the bilayer HTL. After annealing the acidic PEDOT:PSS, the sample was ready for $MAPbI_3$ deposition. The anti-solvent free $MAPbI_3$ precursor formulation was modified from literature[2]. The solution was prepared inside a nitrogen glovebox by dissolving an equal molar ratio of PbI_2 and MAI in 2-MOE (0.8 M) and adding NMP (40 mol% of $MAPbI_3$). The $MAPbI_3$ precursor solution was mixed for at least 3 hrs prior to use. The PEDOT:PSS coated samples and $MAPbI_3$ precursor solution were transferred into a nitrogen purge box with relative humidity ranging between 1% and 3%. The $MAPbI_3$ solution was spin-coated at 5000 RPM for 20 s and then thermally annealed on a hot plate inside the purge box at 100 °C for 10 min. Next, PCBM (20 mg/mL in chlorobenzene) was spin-coated at 1200 RPM for 60 s, followed by spin-coating BCP (0.5 mg/mL in ethanol) at 4000 RPM for 30 s. Finally, 100 nm of Al and 50 nm of Ag were thermally evaporated in a nitrogen glovebox as top contacts. Six 0.11 cm^2 diodes were created on each 1 in x 1 in substrate. The final devices were stored in the nitrogen glovebox, in the dark, over night before device characterization.

Materials and Device Characterization

Scanning electron microscope (SEM) images were taken on a Zeiss Sigma 500 VP SEM with an acceleration voltage of 500 – 1000 V. Atomic force microscopy (AFM) images were taken using an Asylum Research MFP-3D system in tapping mode to determine root mean square surface roughness (σ_{rms}). Average σ_{rms} was calculated from at least three 10 µm x 10 µm areas. Ultraviolet-visible transmission was measured with an Ocean Optics 4000 USB spectrometer. Ultraviolet-visible-near infrared transmission was measured with an Agilent Technologies Cary 5000

Spectrometer. All transmittance data are referenced to air. The average transmittance between 400 and 700 nm is T_{avg} and the average transmittance between 400 and 1200 nm is $T_{avg,NIR}$. Sheet resistance (R_{sh}) was measured with a Bridge Technology SRM-232-100 four-point-probe with ~ 1 mm probe spacings. For small-area samples, R_{sh} was measured five times in the center of each 1 in x 1 in samples. The sample was rotated 45° between each measurement. For large-area samples, both T_{avg} and R_{sh} were measured in nine locations across the 7 in x 8 in sample. IR thermal imaging was taken using a TOPDON TC-001 connected to a Samsung S9 cell phone. Voltage bias for IR thermal imaging was done using a Keithley 2635B source meter.

X-ray photoelectron spectroscopy (XPS) was performed using an Ulvac-PHI VersaProbe2 with a monochromatic Al Kα source (1486.8 eV, 50 W, 15 kV) with a 200 μm beam diameter and a 45° angle to the sample. The O 1s, Ag 3d, In 3d, and Zn 2p spectra were averaged over 20 scans with an energy step of 0.1 eV for 20 ms per step and a pass energy of 23.5 eV. The N 1s spectrum was averaged over 100 scans with an energy step of 0.2 eV for 20 ms per step and a pass energy of 187.85 eV. XPS fitting was done using CasaXPS software. All fits used 70:30 mixed Gaussian:Lorentzian functions. A 10 μA neutralizer was used at a bias voltage of 3 V. AgNWs were deposited on glass/ITO and sigma-aldrich PET/ITO and measured to establish the metallic Ag binding energy of 368 eV. The binding energy for each sample spectrum was then shifted to align the Ag $3d_{5/2}$ peaks to 368 eV, as shown below in **Fig. S1(a)**. The normalized XPS results for Ag 3d, In 3d, and Zn 2p are given in **Fig. S1**.

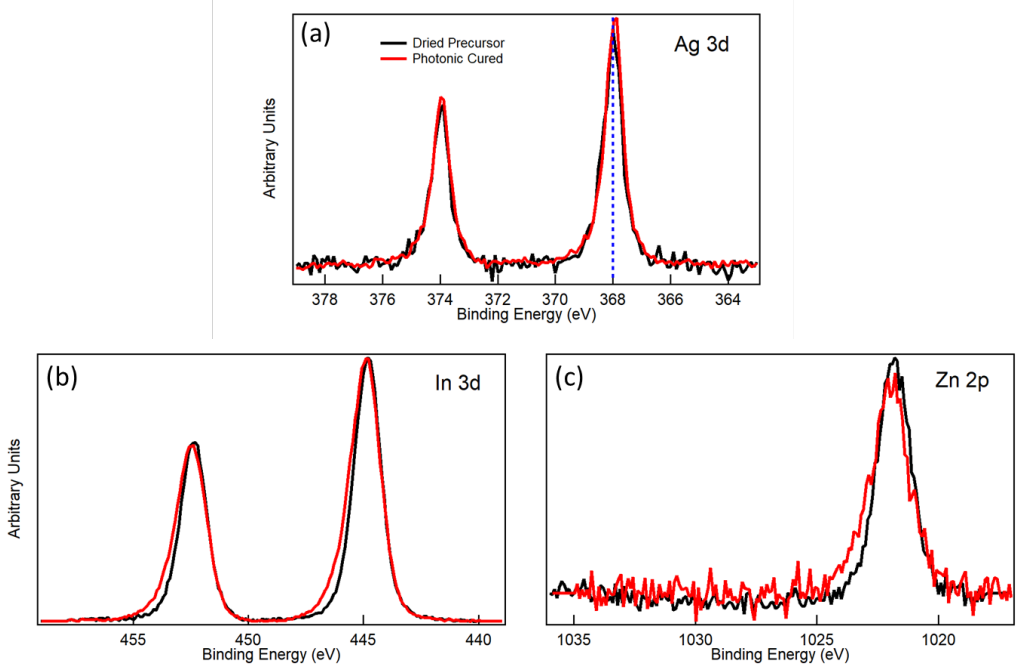

Fig. S1: Normalized XPS spectra of (a) Ag 3d, (b) In 3d, and (c) Zn 2p comparing the dried hybrid TCE precursor (black) and the final hybrid TCE after photonic curing (red).

Thermogravimetric analysis (TGA) was conducted with a TA Instruments Q600 on 5 – 10 mg samples. The indium or zinc nitrate salts were placed directly in a ceramic sample pan. The temperature was ramped from room temperature to 500 °C at a ramp rate of 10 °C/min under 20 mL/min airflow. The TGA data show that indium and zinc nitrate salts completely decompose into indium or zinc oxide at ~ 212 °C and ~ 326 °C, respectively (**Fig. S2**).

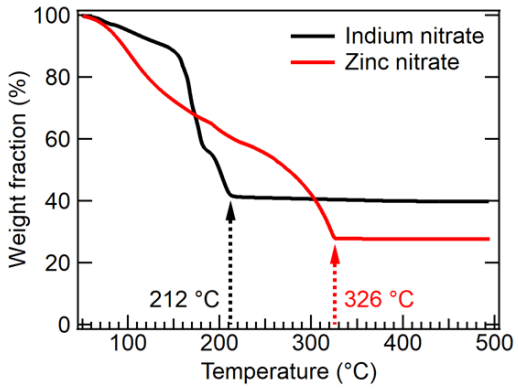

Fig. S2: TGA results of indium nitrate salt (black) and zinc nitrate salt (red).

The current density-voltage (*J-V*) measurements were performed under an AM 1.5G 100 mW/cm^2 AAA solar simulator (Abet) in a nitrogen glovebox using a Keithly 2635A source meter. The illumination aperture size was 0.049 cm^2. The applied voltage was ramped from -0.2 V to 1.2 V for the forward scan and from 1.2 V to -0.2 V for the reverse scan, at a ramp rate of 70 mV/s. Forward- and reverse-scan *J-V* curves (**Fig. S3**) show low hysteresis for champion PSCs made on the hybrid TCEs, regardless of which PEDOT:PSS HTL was used.

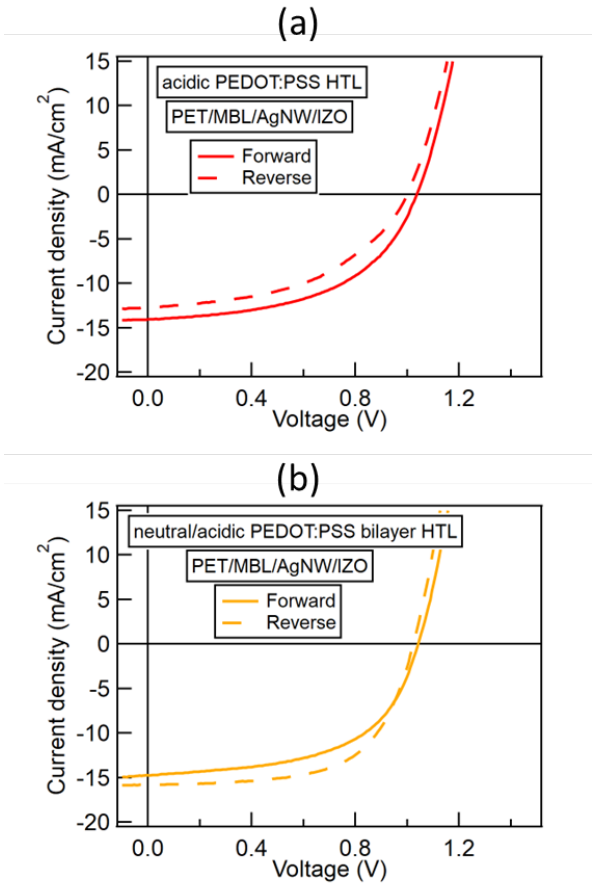

Fig. S3: Forward- and reverse-scan *J-V* curves for champion PSCs made on top of hybrid TCEs with (a) acidic PEDOT:PSS HTL and (b) neutral/acidic PEDOT:PSS bilayer HTL.

Large-area Coating Modifications

The blade-coating procedure for large-area samples is the same as above for the small-area samples, with the following modifications:

- A 175 μm thick PET/MBL substrate was used. The flexographically printed Ag metal lines were ~ 200 nm tall, but otherwise the same as the small-area samples.
- The substrates were cut to 7 in (cross-web) x 8 in (down-web) areas.
- The substrates were only blown with dry N_2 prior to coating, with no other cleaning or preparation steps.
- A Zehntner ZAA 2300 blade-coater was used with an 8 in ZUA 2000 blade-applicator. This blade-coater has an air knife, which is fixed just behind the blade applicator to supply a flow of dry N_2 to the coating surface. The air knife was used to dry the AgNW layer (i.e., the AgNW layer was not dried on a hot plate) but was not used during the IZO coating. Similar to above, the IZO layer was allowed to relax for 90 s and then dried on a hot plate at 90 °C for 2 min.
- The AgNW layer was deposited using a blade-gap of 350 μm and a dispense volume of 230 μL. The IZO layer was deposited using a blade-gap of 275 μm and a dispense volume 170 μL. Both layers were coated at a blade-speed of 30 mm/s.
- The PulseForge Invent used is a roll-to-roll (R2R) system with a web of PET conveying underneath the flash lamp processing area. This PulseForge Invent is equipped with three 950 V lamp drivers, two 15 k W power supplies, and a 20 mm diameter x 300 mm long xenon flash lamp that provides a uniform illumination area of 75 mm x 300 mm. Coated hybrid TCE samples were taped down to the PET web and conveyed at a web speed of 25 cm/min for processing. Pictures of large-area hybrid TCE samples being processed on the R2R photonic curing tool are shown in **Fig. S4**. The photonic curing parameters were adjusted to closely

match the parameters listed above for small-area samples: 410 V pulse voltage, 25 ms pulse envelope, 24 micro-pulses, 45% duty cycle, 9 pulses, 1.2 overlap factor, 25 cm/min web speed, and ~ 3.5 J/cm^2 pulse fluence. The overlap factor, described in reference [3], number of pulses, and web speed determine how many times a specific point on the sample is pulsed. The overlap factor mitigates flash lamp intensity drop near the edges of the illuminated area. An overlap factor of 1.2 equates to an overlap of 17% between pulses.

Fig. S4: Images of hybrid TCEs just after being conveyed through the R2R photonic curing tool. The flash lamp is enclosed in the black box, labeled PulseForge Invent, in the left image.

The TCE thickness was measured by laser scribing to create a step and then measuring with optical profilometry. **Fig. S5** shows a picture of a laser-scribed hybrid TCE sample. Optical profilometry was done with a Bruker Contour GT white light interferometer using a 20x objective lens and VXI mode after the sample was coated with 25 nm Au.

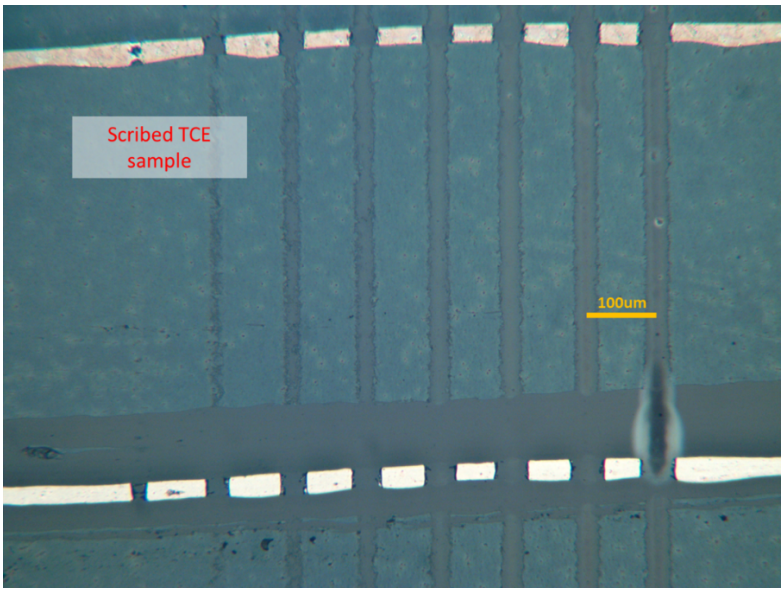

Fig. S5: Laser scribed hybrid TCE sample.

References

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3. Schroder, K. A., Martin, K. M., Jackson, D. K. & McCool, S. C. Method and Apparatus for Curing Thin Films on Low-temperature Substrates at High Speeds. (2013).